RESEARCH PAPER NUMBER THIRTY-FIVE

APPLICATION OF THE PRINCIPLE OF DISPERSION TO PORTLAND CEMENT

BY

EDW. W. SCRIPTURE, JR., PH. D.

DIRECTOR

Master Builders Research Laboratories

CLEVELAND, OHIO

FOREWORD

ENGINEERS, architects and those connected with the various phases of construction are well acquainted with the many improvements made in the manufacture of portland cement since its introduction. They are familiar with the facts that better design of mixes and more care in the selection of aggregates have vastly increased the quality of concrete and mortar, but they are also aware that an important problem having to do with durability and the other properties of concrete remained to be solved: *the reduction of excess water necessary to place all concrete.* Leading investigators have seen the vital need for this improvement while observing the performance of concrete during and after placement in many existing structures, and also in the upkeep costs of structural repairs of railroads, utilities and other large industrial organizations.

The Research Laboratory of The Master Builders Company recently announced a new principle for the improvement of concrete and mortar—Cement Dispersion. They have spent ten years in proving that by adding to the concrete or mortar mix *a cement dispersing agent* the basic problem of all cement mixes is attacked, namely, *the excess water required for placeability.* Reduction of this water insures improvement of the properties of the structure with respect to durability, watertightness, strength and other important qualities.

The Master Builders Company feeling that the introduction of this discovery and its application to practical construction will be welcomed by everyone connected with the building industry has published this paper. The following pages set forth the manner in which dispersing agents function in colloidal systems generally, and describe the way in which this principle has been applied to cement for the improvement of concrete and mortar.

APPLICATION OF THE PRINCIPLE OF DISPERSION TO PORTLAND CEMENT

INTRODUCTION

PORTLAND Cement is an extremely versatile material admirably adapted to a great variety of applications. Its ability to be placed, mixed with aggregate, in the form of a plastic mass into any desired shape and subsequently to harden in that shape make it a means for carrying out operations of construction which could not readily be accomplished in any other way. Its low cost makes feasible structures which could not otherwise be attempted.

In its very strength lies its greatest weakness. To make a plastic mass from portland cement and aggregate, either mortar or concrete, it is necessary to add water. Part of this water is required to combine with the cement but the greater part of it serves no other purpose than to make the mix placeable as has been stated by Mr. P. H. Bates:—[1]

"Since the amount of water required to produce the hydration accompanying maximum development of strength is much less than that used in dry mixes of concrete (somewhat less than 18 pounds of water per bag of cement are needed to produce a decidedly 'complete hydration': this is less than half the amount used in a 4.5 gallons per bag mix, usually considered a very dry mix), it can be realized that a very large part of the mixing water should really be called 'placing' water, and is needed to get the concrete to where it is desired that it should harden. We are, therefore, attaining a strength less than the potential strength and in so doing also materially affecting adversely the properties of volume change and durability."

Many attempts have been made to overcome the inherent disadvantages from which portland cement suffers. These have taken various forms. Chemical reagents, such as calcium chloride, have been added to change the rate of the hydration reaction. Modifications have been made in the composition of the cement itself. In general such measures have produced certain results with respect to acceleration, retardation or similar properties but they have not had any significant effect in solving the basic problem of eliminating or reducing the excess water. In order to overcome the tendency, directly attributable to excess water, of the concrete to absorb water, waterproofing ingredients of the water-repellant or stearate type have been introduced. These have served a useful purpose under some conditions, particularly where no hydrostatic pressure was involved, but have not attacked the

[1]Trends in the Production and Use of Various Types of Hydraulic Cements by P. H. Bates, J. Am. Con. Inst., Jan.-Feb. 1935.

fundamental problem. Pozzuolanic materials have been employed to improve corrosion resistance but these have had to compete with the increase in water necessitated by their addition to the mix. Other finely divided powders have been incorporated in concrete mixes for reasons which were not always clear but usually with the idea that workability would be improved. Such materials defeat their own purpose because, far from reducing the amount of water required for a given consistency they have had precisely the opposite effect. This situation has been summarized by Mr. F. R. McMillan:—[2]

"It can be stated as a general rule that an increase in the necessary water content of the cementing paste in concrete is detrimental. It follows, therefore, that any beneficial effect which an admixture may have must compete with the detrimental effect of any increase in the water content which its use may incur. This holds for portland cement as well as for other powdered materials. For example, to add cement only to the mix will increase the strength to a greater degree than to add the same amount of cement together with water. The fact that the addition of cement plus water may show an increase in strength merely illustrates that the detrimental effect of the added water did not offset the beneficial effect of the added cement."

The many expedients which have been tried, whether production of special cements by altering the composition of the cement itself or additions to the cement or the mix, have produced, in many cases at least, desirable results in some particular direction. They have not, however, been effective in attacking the underlying cause of most of the weakness of concrete or mortar; the excess water required to make the mix placeable. It would appear that any radical improvement in the properties of concrete or mortar should be sought in the reduction of this 'placing' water. Actually much of the investigational work on concrete has been direct to this end through mix design, selection of materials, methods of handling and similar means. As pointed out by Mr. McMillan[3] the benefits to be derived by these expedients are small:—

"At best, only a bare 5 per cent of the concrete volume in plastic mixtures can be changed from water into solid material by improvements in grading over what is ordinarily accomplished. This leaves from 8 to 12 per cent of water, as shown in the figures. It is toward the reduction of this quantity of water that any proposed improvements must be directed."

Accepting cements as they are now produced and assuming that every available advantage has been taken of the best methods of mix design and concrete handling, there still remains a wide gap between the properties of the concrete produced and the potential optimum. The most promising approach to a means of closing this gap lies in a study of the water-cement paste as a colloidal system and the application to it of physico-chemical principles, particularly that of dispersion.

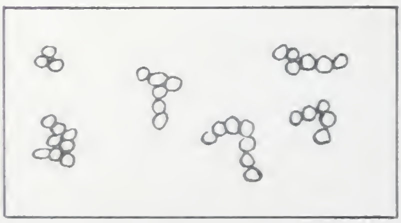
[2]A Method of Evaluating Admixtures by F. R. McMillan and T. C. Powers J. Am. Con. Inst., April, 1934.

[3]Basic Principles of Concrete Making—By F. R. McMillan, Pg. 65.

DISPERSION IN A LIQUID MEDIUM

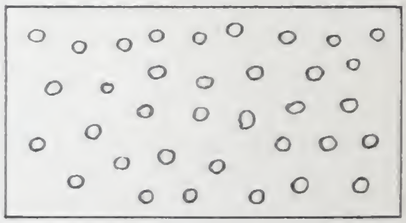
When incorporated in an aqueous medium the particles of a solid tend to agglomerate and act as large clumps rather than as individual particles (Fig. 1). This is known as a flocculated condition and is due to the absence of electrostatic charges on the particles so that when they collide they tend to stick together. If a dispersing agent is incorporated in the flocculated solid-liquid system then the agglomerates or clumps tend to be broken up and the solid particles are distributed more or less evenly through the aqueous medium in the form of individual or discrete particles. The system is then said to be deflocculated or dispersed (Fig. II). The action of the dispersing agent is caused by its orientation with respect to the solid particles whereby these are endowed with electrostatic charges of like sign so that when they collide they are mutually repelled and do not tend to stick together. This effect may also be enhanced by the action of the dispersing agent as a protective colloid which prevents the particles coming in close contact with one another.

Fig. I.



Flocculated

Fig. II.

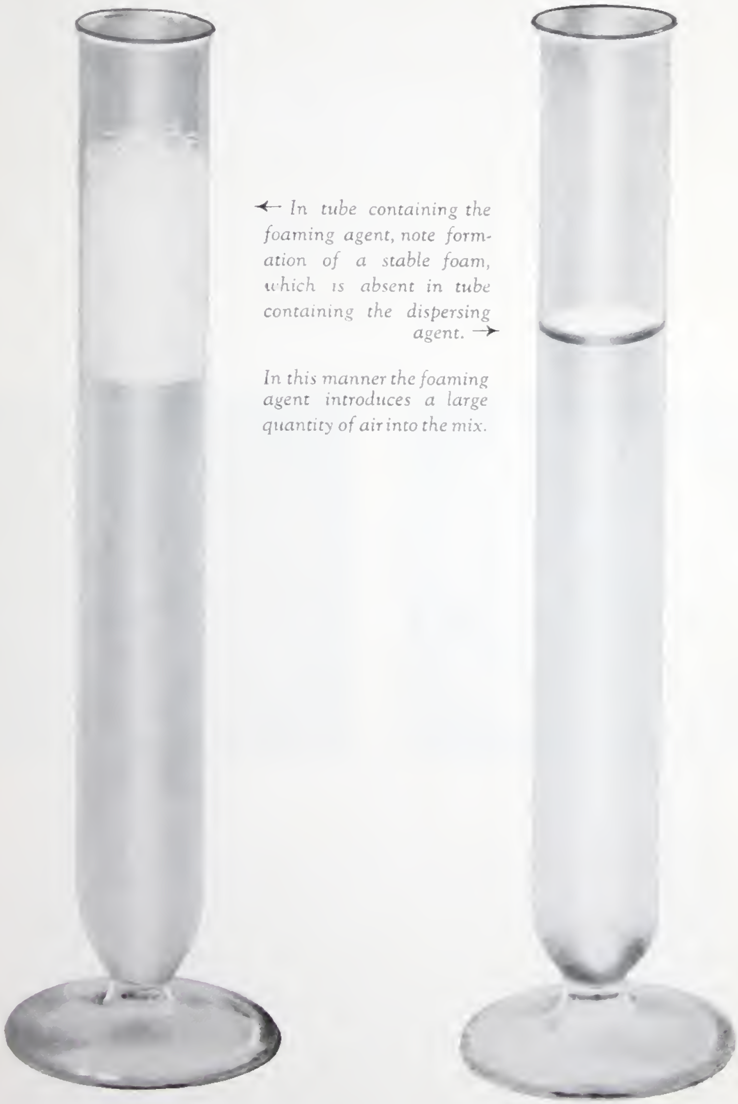


Dispersed

Dispersing agents are specific in their nature, that is, a dispersing agent for one solid-liquid system may or may not be a dispersing agent for some other liquid-solid system. What reagent or reagents will act as dispersing agent for one particular system depends on the absorption relations between the dispersing agent and the system and will be determined by experiment. Dispersing agents, moreover, should not be confused with wetting agents, emulsifying agents and other surface active compounds*. Wetting agents are compounds which reduce the surface tension of water and thereby reduce the interfacial tension between the water and the solid which is to be wet. Emulsifying agents are compounds which concentrate at the interface between the continuous and the emulsified or dispersed phase due to the solubility relations of the two parts of the molecule. While these reagents may appear to have some of the characteristics of dispersing agents they are not dispersing agents and do not produce the same results. Furthermore, these wetting and emulsifying agents tend to cause foaming and may introduce other extraneous effects in any particular system.

*Fig. III—(See page 7.)

Fig. III



← *In tube containing the foaming agent, note formation of a stable foam, which is absent in tube containing the dispersing agent.* →

In this manner the foaming agent introduces a large quantity of air into the mix.

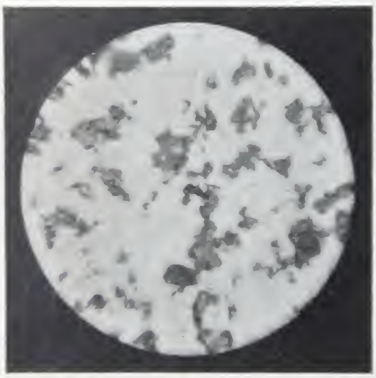
Foaming Agent | Dispersing Agent

DISPERSION OF PORTLAND CEMENT

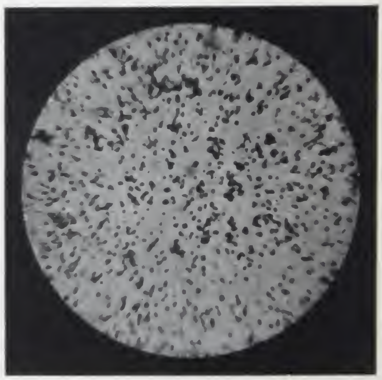
The operation of dispersing agents has been known and utilized for a long time with respect to some applications as for example, in the ceramic industries for the deflocculation of clay slips. Until recently no dispersing agents have been known which were applicable to the deflocculation of portland cement. Recent researches have shown that certain complex organic compounds will disperse cement and will not have injurious effects such as a marked lowering of surface tension causing foaming or interference with the hydration reactions of the cement.

The action of a cement dispersing agent on portland cement in water is similar in its effects to the action of any dispersing agent in a solid-liquid system. Fig. IV shows photomicrographs (a) of cement in water in its normal or flocculated condition and (b) of cement in the dispersed condition, produced by adding a small amount of dispersing agent to the water.

Fig. IV



UNDISPERSED



DISPERSED

The dispersion or deflocculation of portland cement in a concrete or mortar mix is important in a number of aspects. In general it may be pointed out that the reactions on which portland cement depends for its valuable properties are surface reactions. They are, therefore, a function of the surface area of the cement. For this reason cement manufacturers have consistently increased the fineness of grinding of cement clinker. Unfortunately the full surface area produced by fine grinding is not available for reaction due to the flocculated condition of the cement in the mix. It is perhaps even more unfortunate that this agglomerating tendency is even greater with greater fineness so that the beneficial effects of fine grinding have been in some measure offset by the formation of clumps. The addition of a dispersing agent to portland cement mixes has made available for reaction for the first time the full surface area of the cement particles. A dispersing agent in a cement mix, therefore, permits utilization of the cement to the full extent.

A special field is that of colored concrete or mortar mixes. To produce color in a concrete structure suitable pigments are incorporated in the mix with the cement and in some cases colored aggregates are used. In such an application a cement dispersing agent offers not only advantages in relation to the properties of the concrete or mortar but it also effects improvements with respect to the pigment itself. The presence of the dispersing agent facilitates the dissemination of the pigment uniformly throughout the mix, increases the brilliance of the resulting color, produces equal color with less pigment (incorporation of any fines including pigments has an adverse effect on the properties of the mortar since the water requirement of the mix is increased), and overcomes the deleterious effects of many pigments.

Fig. V

EFFECTS OF DISPERSION ON THE PROPERTIES OF CONCRETE AND MORTAR

Since the properties of concrete and mortar are primarily dependent on the amount and quality of the cement paste any influence which alters the nature of this paste will inevitably influence the properties of the mix. Dispersion of the cement basically changes the relations of the solid particles to the liquid in this colloidal system and consequently may be expected to have a profound influence on many if not all of the characteristics of the concrete or mortar. These effects may be divided into two groups corresponding to the two states in which concrete exists: the transitory plastic stage during placing and the ultimate hardened mass.

A.—Effects of Dispersion During Plastic Stage

The plastic state is vitally important because this is the period during which the concrete or mortar is placed to fill the space which it is to occupy, compacted, and finished. Unless the mix is workable at this time, a sound structure will not be produced regardless of any other properties of the mix. This property of workability may be considered as made up of two components: mobility or ease of flow and cohesiveness or resistance to segregation.

Dispersion of the cement particles will increase mobility or ease of flow. This is because the water held in the clumps or agglomerates of the flocculated cement is released to become a part of the fluid medium through which the particles move. Further by breaking up these

Fig. VI

UNTREATED MIX		DISPERSED MIX
6½ gals.	W/C	6½ gals.
1 in.	Slump	5 in.

clumps the size of the units in the liquid is reduced so that they can move more easily past each other in the fluid. The result is a more workable concrete which is more easily handled, or placed with less danger of the defects commonly due to lack of workability. What is perhaps even more important is that this permits a more workable mix to be produced with less water, that is, at a lower water cement ratio.

Cohesiveness is attributable to the attractive forces between surfaces. Therefore, dispersion of the cement which makes available a greater surface area will increase the cohesiveness of the mix[1]. A first result is that the mix becomes more "fatty" or "buttery" which is extremely important in some types of work. An even more generally important effect is a reduction of the tendency of the components of the mix to separate, that is, toward segregation. The aggregate is less apt to separate from the cement paste so that the danger of honeycombing, sand streaking and similar defects is minimized. In its upward movement through the mix the water tends to collect under the larger pieces of aggregate forming pockets on the underside such that the aggregate is not bonded to the cement paste. The pockets constitute points of weakness and of attack by destructive agencies. Separation of the water and fines in an upward direction from the coarser part of the mix is prevented. By this means 'bleeding' or 'watergain' and the formation of laitance are eliminated or reduced. The uniformity of the mix in place is enhanced. (Fig. VII—see page 12).

A further effect of dispersion, also due to the greater surface area available, is a greater force holding the water to the cement particles. This produces higher "water retentivity" which is particularly important in masonry mortars where porous masonry units tend to suck water out of the mortar. It is also important in other mortars and concrete as it retains the water in the mass promoting better curing.

One phenomenon which occurs in concrete and mortar during the plastic stage has been rather neglected. This is the volume change or more specifically shrinkage which occurs before hardening. The volume changes which occur at this time are in all probability more important

(1) This does not contradict the previously made statement that the dispersion of the cement particles is due to the repellent action of like electrostatic charges. This repulsion which effects dispersion refers to the forces between the cement particles. The attraction which operates in connection with cohesiveness refers to the forces between the cement particles and the other components of the mix, particularly the aqueous medium in which the cement particles are dispersed. Since the water does not carry an electrostatic charge there is no repulsion between it and the cement particles: hence the attractive forces between the water and the solids in the mix are dependent on surface area of the solids.

Fig. VII

← *In the flocculated condition the solid particles settle to the bottom leaving clear water at the top; a condition analogous to water gain.*

The dispersed particles remain suspended. →

UNTREATED (Flocculated)

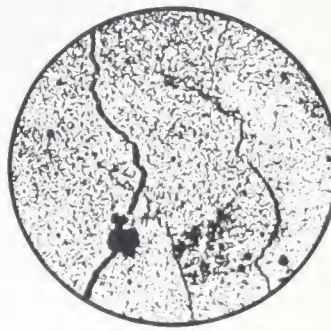
TREATED (Dispersed)

than those which take place subsequently[2]. They are caused by movement of water from one part of the mix to another and by loss of water from the mix by suction, by evaporation or by other means. Such volume changes produce incipient or actual cracks which impair the integrity of the structure and make it susceptible to subsequent attack. (Fig. VIII). Dispersion of the cement counteracts these volume changes, first by reducing the amount of water required for a workable mix and second by imparting higher water retentivity thus resisting movement and loss of water.

Fig. VIII

CRACKS IN UNSTRESSED CONDITION

Photomicrographs show how cracks due to shrinkage open wider and new cracks appear with application of loads.



CRACKS WHEN LOAD IS APPLIED

(2) "The occurrence of cracks during the 'pre-set' period is so frequent, especially in flat work, it is surprising such little mention has been made of it in concrete literature. Yet positive, or even incipient, cracks produced in this pre-set period are often more dangerous to continuity than those produced by the normal drying out after the cement has become hard set.

When screeding of flat work or rodding and vibration of concrete in forms is completed, all solid particles settle slowly at a uniform rate until the coarser particles become arched and fixed in the mass. Each smaller size will then stratify until it in turn touches other particles. This settling action exposes water at the surface which proceeds to evaporate in the presence of dry air, warm weather, and wind, singly or combined. The structure formed by the settlement of the solids to a rigid condition is rather loose and the smaller particles are still far from consolidated, being held apart by the water films on their surfaces.

As the mixture dries out, the contained water moves through the mass to the drying surfaces and may cause further readjustments. When drying has proceeded beyond the point of particle adjustment, air is drawn into the mass to replace the volumes in the voids formerly filled with water. From this stage on to the final drying or to some point before hard set, surface tension plays its part in the shrinkage of the mass."

C. A. G. Weymouth—J. Am. Con. Inst., Sept., 1940, Supplement Section 1.
Pg. 540-2 Pg. 540-3

The effects of dispersion of the cement particles on plastic concrete or mortar may be summarized as follows:—

1. More placeable concrete with less water.
2. Increased fattiness.
3. Reduced segregation and bleeding.
4. Greater water retentivity.
5. Reduced shrinkage before hardening.

B.—Effects of Dispersion on Hardened Concrete or Mortar

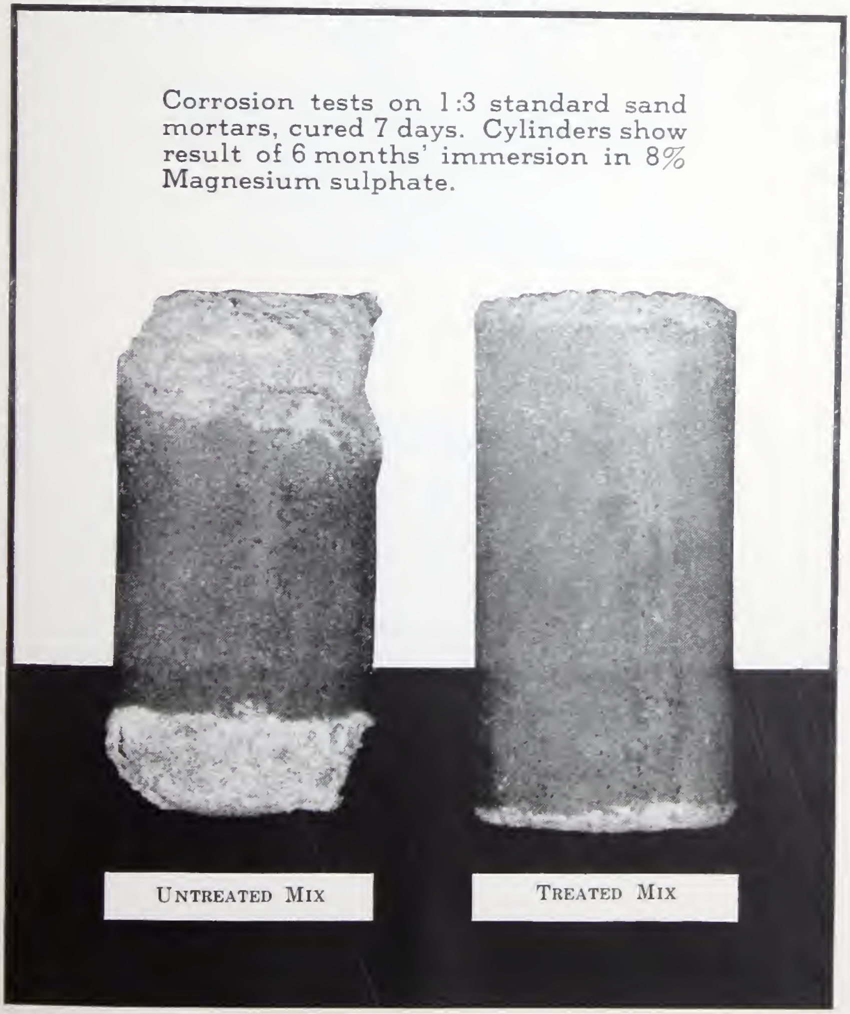
Dispersion affects practically all the important properties of the hardened concrete or mortar. This is due primarily to two causes. First, the reduction of the amount of water required in the mix produces the well-known beneficial effects of reduced water-cement ratio and reduced water per unit volume. (Fig. IX). Second, the dispersion of the cement particles produces a finer grained structure in the cement paste and an increased surface area such that the hydration reactions of the cement will proceed more effectively and more efficiently. Some of the more important properties may be considered in somewhat more detail.

Fig. IX

UNTREATED MIX		DISPERSED MIX
$5\frac{1}{2}$ gals.	W/C	$4\frac{1}{2}$ gals.
$1\frac{3}{4}$ in.	Slump	$2\frac{1}{2}$ in.

Durability — Durability means the ability of the structure to resist destructive agencies. These are commonly corrosive solutions and freezing and thawing. Since the attack of corrosive solutions is a reaction occurring at the surface where the solution comes in contact with the cement the rapidity of attack is dependent primarily on the ability of the corrosive solution to penetrate into the structure, secondarily, on the ability of the cement itself to resist attack. The ability of the solution to penetrate is governed by the same factors which contribute to watertightness. Hence, a dispersing agent increases resistance to corrosion. (Fig. X).

Fig. X



Disintegration by freezing and thawing is also primarily dependent on the ability of water to penetrate into the concrete where it will freeze, expand and break down the structure, secondarily, on the strength of the cement paste to resist this force. Since a dispersing agent reduces permeability and in other ways makes the concrete more water-tight and since it also increases strength, it will markedly increase resistance to freezing and thawing. (Fig. XI.)

Fig. XI

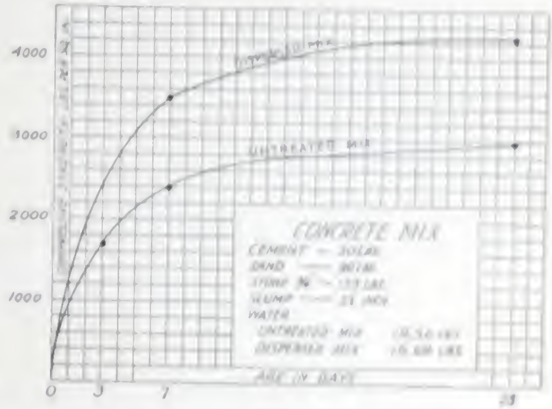
UNTREATED CONCRETE - 150 CYCLES OF FREEZING AND THAWING, LOSS IN WEIGHT - 73%.

DISPERSED CONCRETE, SAME DESIGN AND CONSISTENCY, 150 CYCLES OF FREEZING AND THAWING - LOSS IN WEIGHT - 10%.

Watertightness — Watertightness is dependent on freedom from gross defects, freedom from cracks and on permeability. Since the use of a dispersing agent, as previously discussed, results in an improvement in all these respects it will increase watertightness.

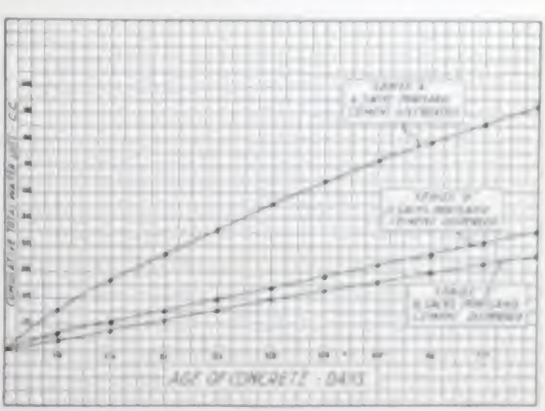
Strength — Strength is dependent on water cement ratio so that strength will be increased by the reduction of water made possible by dispersion. The greater surface area made available by dispersion also leads to greater and more rapid hydration so that further improvements in strength are secured.

Fig. XII



Permeability and Absorption — Permeability and absorption are proportional to the volume of excess water per unit volume of concrete. The reduction in the excess water required for workability by the use of a dispersing agent therefore reduces permeability and absorption.

Fig. XIII



Plot of Permeability Test Data

(Test specimens held under a pressure equivalent to a 60 ft. head of water for 24 hours, for each day shown).

Volume Change — Volume change or shrinkage is proportional to the volume of cement paste per unit volume of concrete, that is, the volume of cement plus the volume of water. Reduction in the water then reduces volume change.

Uniformity — The uniformity of the hardened structure and freedom from gross defects will be improved due to the improvement in the properties of the plastic mix as described previously.

The effects of a dispersing agent on the properties of the hardened concrete or mortar may be summarized as follows:—

1. Increased durability and longer life.
2. Increased watertightness.
3. Higher strength.
4. Lower volume change.
5. Lower permeability or absorption.
6. Greater uniformity and freedom from gross defects.

CONCLUSION

The basic reason that concrete and mortar do not realize the full potential qualities which are warranted by the inherent characteristics of portland cement lies chiefly in the excess water required for placeability. Any improvements to be expected in the properties of concrete will naturally follow from methods which permit this excess water to be reduced. An attack on this problem has been made from the point of view of a study of the physico-chemical characteristics of the cement-water paste. The result of this work has been the application of the principle of dispersion to the system.

A cement dispersing agent radically alters the physical nature of the paste in such a manner that placeability can be attained in concrete and mortar with a substantial reduction in the water required. This in turn has profound effects with respect to improvement of durability, watertightness, strength, volume change and other properties.

It will be realized that this principle of cement dispersion is applicable to concrete and mortar generally. Since the many applications of cement mixes require some variations in the properties of the different mixes, some modifications of or additions to the cement dispersing agent may be desirable, but the principle of reduction in water by means of dispersion will remain universally beneficial wherever cement is used.

Master Builders Research Laboratories
Cleveland, Ohio

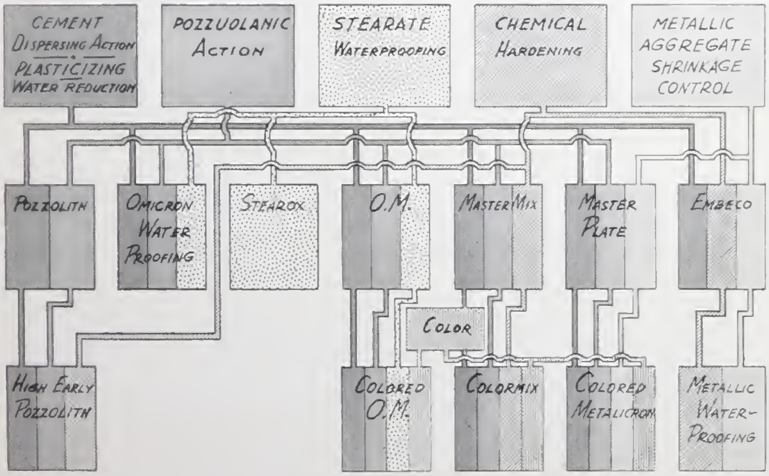
MASTER BUILDERS PRODUCTS EMPLOYING THE CEMENT DISPERSION PRINCIPLE

The principle of dispersion of cement is applicable to any type of work involving cement in mortar or concrete. This work is of a very varied nature and for different applications somewhat different properties are required. To accomplish this purpose the cement dispersing agent may be combined with other basic principles for the improvement of specific properties of concrete and mortar, as illustrated by the diagram below. These include pozzuolanic activity, stearate waterproofing, chemical hardening, and metallic aggregates.

The Master Builders Company has developed a group of products adapted to various specific concrete and mortar applications. The exclusive dispersing agent is incorporated in each of these products in a manner to impart the maximum effect on the resultant structure. These products are as follows:

Application	*Product*
Concrete (General)	Pozzolith
High Early Strength Concrete	High Early Pozzolith
Concrete (Exposed to Capillary Moisture)	Omicron Waterproofing and Stearox
Floors — Heavy Duty	Masterplate
Floors — Light Duty	Mastermix
Colored Floors	Colored Metalicron and Colormix
Brick Mortar	Omicron Mortarproofing ("O. M.")
Colored Brick Mortar	Colored Omicron Mortarproofing
Grouting and Maintenance	Embeco and Metallic Waterproofing

PRODUCT COMPOSITION DIAGRAM



MASTERBUILT PRODUCTS

TRADE MARK

THE MASTER BUILDERS COMPANY

Factories in Cleveland and Buffalo

CLEVELAND, OHIO

Sales Offices in All Principal Cities